An efficient and general analytical approach to modelling pyrolysis kinetics of oil shale

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HIGHLIGHTS

- Novel approach to analytical modelling pyrolysis kinetics of oil shale is presented.
- The methodology is generic which can model many types of reaction kinetics.
- The model is efficient, accurate, easily implemented and application-independent.
- Comparison with measurements and numerical simulations shows excellent agreement.
- Favorable generalizations and extensions of the modelling approach are presented.

ARTICLE INFO

ABSTRACT

This paper presents a new approach to analytical modelling pyrolysis kinetics of oil shale based on Arrhenius equation which is inherently nonlinear allowing no exact analytical solution. The proposed method introduces an approximation which leads to a significant simplification of the closed-form solution and the calculation and allows for rapid estimates of kinetic parameters. The analytical model is successfully validated by both experimental data and the numerical model ($R^2 > 0.99$). In addition, the developed methodology and model are sufficiently general which can be applied to other types of fuel resources and chemical reactions. To demonstrate, some generalizations and extensions of representative kinetic models in wide-area applications are presented. The proposed modelling approach improves over the state-of-the-art methods for pyrolysis kinetics models in its efficiency, simplicity, generality and application-independence. The model is easy to implement and computationally attractive.

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1. Introduction

As an energy source, oil shale pyrolysis has been produced over hundreds years through heating the oil shale to a temperature that the kerogen, the organic portion of the oil shale, decomposes into gas, oil and coke [1,2]. Broadly, two basic oil shale retorting processes, in situ (underground) and ex situ (aboveground), are used. Both techniques require energy to heat the oil shale to pyrolysis temperature. Modelling the pyrolysis kinetics of oil shale for an understanding of the decomposition mechanisms and kinetic parameters are significant for designing and operating an energy efficient pyrolysis process because pyrolysis is a very complicated thermochemical conversion process involving extremely complex reactions and the end products depend on numerous factors [3]. Hence, despite extensive knowledge of the process, an exact mechanism and kinetic modelling for oil shale pyrolysis is difficult or practically impossible. Therefore, many comprehensive pyrolysis models are based on Arrhenius-type kinetic equation for interpreting fundamental mechanism of the entire pathway or specific mechanisms within the pathway. Arrhenius model has a long history of use as pyrolysis kinetics and revisiting the mechanisms for pyrolysis and the relevant models so far developed demonstrate its generality which has proven to be a valuable analysis tool with wide applications [3–8].

Arrhenius kinetics for decomposition is modelled based on the two most important and frequently used parameters: activation energy and pre-exponential factor (e.g. [4]). Since an accurate Arrhenius model equation is inherently nonlinear in nature allowing no exact analytical solution, numerical techniques become necessary to find the solutions and the parameters (e.g. [9]). The underlying mechanisms remain elusive with numerical approaches.

The analytical model, on the other hand, has an advantage that it can provide a clear description of the primary kinetics and parameters for the underlying mechanisms. It is suited to understand the outcomes and to interpret the experiments. Extensive analyses, therefore, have been performed to explore thermal decomposition kinetics and to determine kinetic parameters for pyrolysis kinetics of oil shale as well as for biomass using analytical models (see, for example, [10,11], for general reviews). Two basic principles regarding the methodology can be identified among the analytical models: integral and differential methods based on Coats–Redfern [12] and Friedman [13] approaches and their modifications [6,14–16]. Typically, Thermogravimetry (TG) and Differential Thermal Analysis (DTA) experiments are conducted under either isothermal or non-isothermal condition. The TG/DTG data are analyzed and the kinetic parameters are adjusted based on the kinetic model equation using goodness-of-fit assessment [17]. Graphical methods are often used to evaluate goodness-of-fit.

Although simple, an obvious disadvantage with these methods is that it describes observations of the data only without showing the underlying mechanism by which the data are produced. Another relevant disadvantage which is directly tied to this is that graphical methods generally suffer from poor statistical properties (see, for example, [10]). Attempts have been made to improve these methods and majority of the improvements are made to better approximate the Arrhenius temperature integral (see [4,6,18,19] for a general review). The temperature integral is always encountered which permits no analytical solution. The approximation of the temperature integral is usually done through predefined formula, which is undoubtedly related to the unknown kinetic mechanisms. Accuracy is often sensitive to the form of the assumed kinetic mechanisms [6,20,21], which presents a major challenge in kinetics analysis. This requires prior knowledge of the kinetic mechanisms which is often inaccessible in practice.
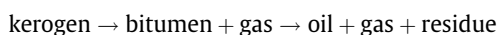
This paper presents a new analytical methodology to address such an issue to improve upon past analytical models. We approach the temperature integral problem differently than existing models in that the proposed model does not make any assumptions on the temperature integrals or kinetic mechanisms. The developed model provides a closed-form expression of the decomposition kinetics based on kinetic parameters. Experimental and numerical validations show an exceedingly high accuracy of the model ($R^2 > 0.99$).

One significant aspect of the developed modelling method is the straightforward formalism for the final model solution which represents a significant simplification of the closed-form solution and calculation and allows for rapid estimates of kinetic parameters. The proposed approach is highly efficient, simple, accurate, yet universal which can be easily modified and extended to accommodate other reaction kinetic features. To demonstrate, we present its generality and practicality through representative wide-area applications and show that many popular existing models can be expressed as instances of our model. Therefore, although the paper concentrates on oil shale pyrolysis, the proposed methodology will be of great interest to researchers and engineers for modelling other types of chemical reactions for fuels [22]. Finally, the implementation is extremely simple which can be achieved with a few lines of code or with spreadsheets or even with a pencil and paper.

2. Methods

2.1. Kinetic model

The kinetics of kerogen decomposition to shale oil is described in two steps [23,24]:

kerogen → bitumen + gas → oil + gas + residue

and modelled as an *n*-order reaction equation [25] for retorting process

$$\frac{dX}{dt} = k(1-X)^n \tag{1}$$

where X is the weight loss or mass fraction or conversion (%) defined as

$$X = \frac{w_0 - w_t}{w_0 - w_f} \tag{2}$$

w_0: initial weight;
w_t: weight at time t;
w_f: final weight;
k: rate coefficient given by Arrhenius equation:

$$k = A \exp\left(-\frac{E}{RT}\right) \tag{3}$$

A: pre-exponential factor;
E: activation energy;
R: gas constant;
T: temperature.

Assuming a constant heating rate $\beta = \frac{dT}{dt}$, an integration of Eq. (3) results in a plot of $\ln\left(-\frac{\ln(1-X)}{T^2}\right)$ or $\left(\ln\left(\frac{1-(1-X)^{1-n}}{(1-n)T^2}\right)\right)$ if $n > 1$ against $1/T$ being a straight line. The kinetic parameters are determined using its slope and intercept. This graphical method is based on Coats–Redfern method which is the most commonly used parameter estimation approach. Despite of ease of use, graphical method has some limitations as described in Section 1. In the following we propose a new model to overcome these limitations.

2.2. The proposed approximate analytical model

Assume $n = 1$. As we'll see later that this assumption is for a simple illustration only and the reaction order is not limited to linear one. Since a constant heating rate $\beta = \frac{dT}{dt}$ is the most common case in applications, Eq. (1) leads to

$$\frac{dX}{1-X} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \tag{4}$$

Integration of Eq. (4) gives

$$\int_{X_0}^{X} \frac{dX}{1-X} = \int_{T_0}^{T} \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT;$$

$$-\ln(1-X)\Big|_{X_0}^{X} = \frac{A}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT \tag{5}$$

The right-hand integral cannot be calculated analytically. We propose its approximation as follows:

$$\int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT = \frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right)\Big|_{T_0}^{T}$$

$$-\int_{T_0}^{T} \frac{2RT}{E} \exp\left(-\frac{E}{RT}\right) dT \tag{6}$$

Rearrange of the terms containing integrals together leads to

$$\int_{T_0}^{T} \left(1 + \frac{2RT}{E}\right) \exp\left(-\frac{E}{RT}\right) dT = \frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right)\Big|_{T_0}^{T} \tag{7}$$

For a small temperature change ΔT, $1 + \frac{2RT}{E}$ is approximately constant. Therefore, Eq. (7) can be approximated as

$$\int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT \approx \frac{\frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right)}{1 + \frac{2RT}{E}} - \frac{\frac{RT_0^2}{E} \exp\left(-\frac{E}{RT_0}\right)}{1 + \frac{2RT_0}{E}} \tag{8}$$

and Eq. (5) becomes

$$-\ln(1-X) = -\ln(1-X_0) + \gamma_T - \gamma_{T_0}$$

$$\gamma_T = \frac{A}{\beta} \frac{\frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right)}{1 + \frac{2RT}{E}} \quad (9)$$

In summary, the weight loss X can be computed based on the following simple closed-form formula:

$$\ln(1-X_1) = -\gamma_{T_1} + \gamma_{T_0}$$

$$\ln(1-X_i) = \ln(1-X_{i-1}) - \gamma_{T_i} + \gamma_{T_{i-1}}, \quad i = 1, 2, \ldots \quad (10)$$

It can be seen that the proposed model is a systematic approach which is simple, efficient and fully automatic. Extensions of it will be presented later.

3. Results and discussion

This section presents the validation of the developed analytical model against both the measurement and the numerical simulation. The following frequently used performance measures are employed to assess the model accuracy: mean absolute error (MAE), root mean squared error (RMSE), mean squared error (MSE) and coefficient of determination (R^2) defined as

$$\text{MAE} = \frac{1}{N} \sum_{i=1}^{N} |Y_{measured/simulated} - Y_{predicted}|$$

$$\text{RMSE} = \left[\frac{1}{N} \sum_{i=1}^{N} \left(Y_{measured/simulated} - Y_{predicted}\right)^2 \right]^{1/2}$$

$$\text{MSE} = \frac{1}{N} \sum_{i=1}^{N} \left(Y_{measured/simulated} - Y_{predicted}\right)^2 \quad (11)$$

$$R^2 = \frac{\left(N \sum_{i=1}^{N} Y_{measured/simulated} Y_{predicted} - \sum_{i=1}^{N} Y_{measured/simulated} \sum_{i=1}^{N} Y_{predicted}\right)^2}{\left[N \sum_{i=1}^{N} Y_{measured/simulated}^2 - \left(\sum_{i=1}^{N} Y_{measured/simulated}\right)^2\right] \left[N \sum_{i=1}^{N} Y_{predicted}^2 - \left(\sum_{i=1}^{N} Y_{predicted}\right)^2\right]}$$

where the subscripts 'measured/simulated' and 'predicted' present the measured or the simulated and the model predicted quantities and N the total number of the points. After the validation procedure, we'll demonstrate some extensions of the developed model which are considered as most commonly used models in reaction kinetics analysis.

3.1. Model validation against experiment

Firstly, experimental data were collected from the measurement of oil shale samples from Huadian, China. The initial weight of the samples was about 4 mg (density 1570 kg m^{-3}). TG/DTA was conducted for the samples using a Netzsch STA 449C thermal analyzer system (Germany) under non-isothermal conditions of both ambient atmosphere and nitrogen atmosphere (fluxed by nitrogen with a flow rate of 50 cm^3 min^{-1}). TG/DTA provides the precise measure of the mass change in regards to temperature change, which is used in analyzing mass change, thermal resisting properties and reaction velocity in samples. Before the experiment, the TG/DTA instrument was calibrated and the samples were finely ground through a 63 μm sieve to eliminate heat and mass transfer effects during pyrolysis. During the experiment, the heating rate was kept as 10 °C min^{-1} starting from ambient temperature and rising to 800 °C. All the measurements were repeated several times

and showed good reproducibility. For the purpose of validation and verification of the developed analytical model, we will focus on the TG/DTA measures under an air atmosphere. The detailed description of the experiment was provided in [26]. Fig. 1 shows the measurements.

Fig. 2 shows the comparison of the model predictions with the measurements. The difference in temperature between two time periods was taken as $\Delta T = 25$ °C. The model accuracy assessment is presented in Table 1, where model comparison with measurement and numerical simulation data on the basis of MAE, RMSE, MSE and R^2 are reported. These error metrics test the differences between the proposed model and the numerical model as well as how well the developed model fits the measurement. Zero value of MAE, RMSE, MSE and R^2 value of +1 indicate a perfect fit. The predicted weight losses were in excellent agreement with measurements across all these comparison metrics ($R^2 > 0.99$).

3.2. Model validation against numerical simulation

To further test the accuracy of the proposed model, a MATLAB program was developed to simulate the exact model Eq. (1) with $E = 60$ kJ mol^{-1} and $A = 34$ s^{-1}. Different temperature intervals ($\Delta T = 2$ °C, 30 °C, 50 °C) and 0–800 °C temperature range were used for generating the temperature versus weight loss data. Fig. 3 displays the comparison results.

Excellent agreement was obtained between the model and the simulation. For temperature interval $\Delta T = 2$ °C, two curves are nearly identical. Very good accuracy was obtained even when the temperature interval ΔT was chosen as 50 °C. These results validate the applicability of the proposed model. Additionally, estimated activation energy $E = 60.12$ kJ mol^{-1} and pre-exponential coefficient $A = 34.03$ s^{-1} were obtained which are very close to their real values. In the next subsection, we'll present how the kinetic parameters are determined using the proposed analytical model.

3.3. Model extension and discussion

The model can be extended to accommodate more complex features. We will present several of them that are considered as especially important and popular in pyrolysis kinetics studies and show that these models can be expressed as instances of our model.

3.3.1. Higher-order reaction

For any n-order, $n > 1$, reaction, the approximate analytical solution Eq. (10) can be modified (details omit) and weight loss X is extended as the following general and simple formula:

$$\frac{(1-X_1)^{1-n}}{n-1} = -\gamma_{T_1} + \gamma_{T_0}$$

$$\frac{(1-X_i)^{1-n}}{n-1} = \frac{(1-X_{i-1})^{1-n}}{n-1} - \gamma_{T_i} + \gamma_{T_{i-1}}, \quad i = 1, 2, \ldots \quad (12)$$

with $\quad \gamma_T = \frac{A}{\beta} \frac{\frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right)}{1 + \frac{2RT}{E}}, \quad n > 1.$

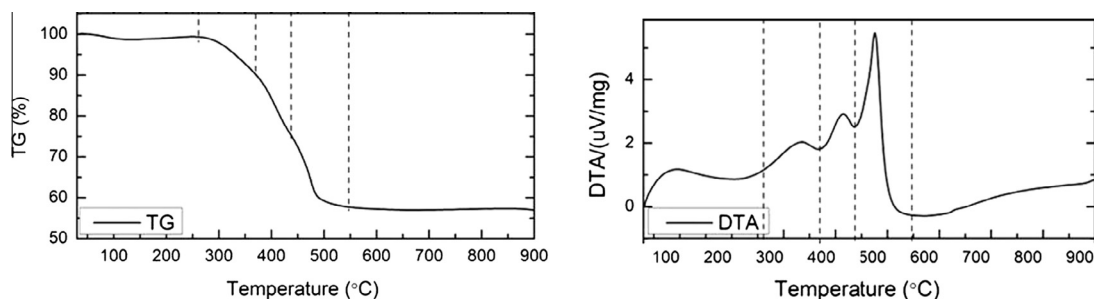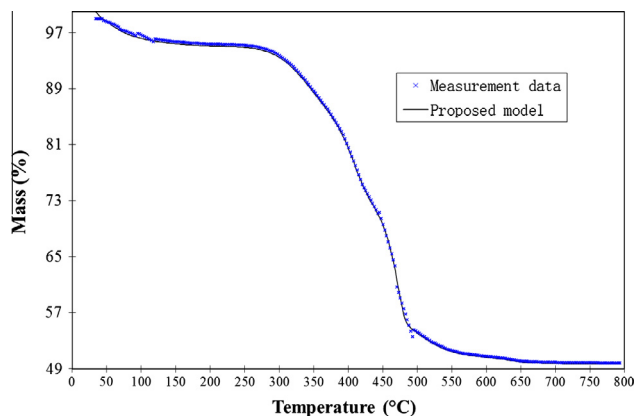**Fig. 1.** TG/DTG measures of the oil shale sample (heating rate 10 °C min^{-1}).

Fig. 2. Comparison of model predictions and measurements.

Table 1

Model accuracy metrics for comparison of the proposed model with measurement data and numerical simulation data.

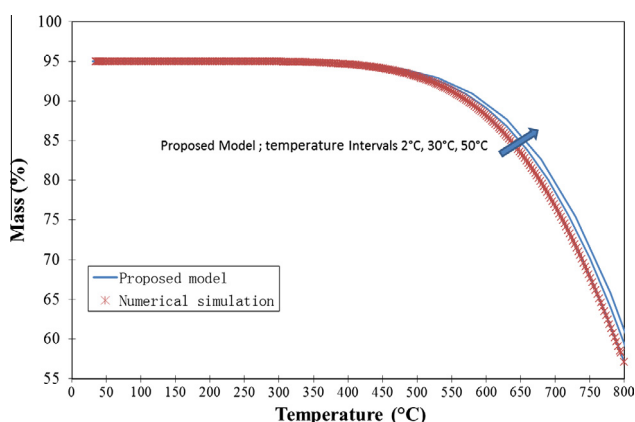| Comparison with	MAE	RMSE	MSE	R^2
Measurement data	0.243	0.280	0.081	0.994
Numerical simulation data	0.001	0.003	0.000	0.998

Fig. 3. Comparison of model predictions and numerical simulations.

3.3.2. Kinetic parameters

Using the analytical model Eq. (10) or Eq. (12) the kinetic parameters of activation energy and pre-exponential coefficient can be easily estimated analytically based on the TG/DTG measurement. Assume $n = 1$ for illustration and consider temperature versus weight loss data $\{T_i, X_{i,0}\}_{i=0,\ldots,N}$ from TG/DTG measurement. Starting from initial values of parameters A_1 and E_1, Eq. (10) is

employed to obtain the simulated data $\{T_i, X_{i,1}\}$ $i = 0,\ldots,N$. The error function is

$$\chi(A, E) = \sum_{i=1\ldots N} (X_{i,0} - X_{i,1})^2$$

The parameter estimates of A and E can be computed or adjusted iteratively by minimizing the error function through generalized reduced gradient method. We found that the iteration converged rapidly. In most calculation cases, only a few iterative steps were needed. Besides, many software programs are available for solving such problems, such as MATLAB's lsqnonlin function in Optimization Toolbox.

To assess the accuracy of the proposed approach we predefined kinetic parameters and applied numerical model to generate the temperature versus weight loss data. Kinetic parameters were estimated with the proposed method and the comparison results are displayed in Table 2. The predefined parameters are listed as 'true' values of the parameters in Table 2. High accuracy was obtained. The estimates are nearly the same as the 'true' values.

3.3.3. Temperature dependent kinetic parameters

In majority of studies the kinetic parameters of activation energy and pre-exponential coefficient are considered to be temperature independent (see all cited papers). However, experiments have suggested that temperature is an important determinant parameters for pyrolysis kinetics and accurate estimates of their temperature dependence are critical to understanding thermal activation processes [27]. However, classic graphical methods cannot unambiguously measure and estimate their temperature dependence due to the mathematical impossibility [27].

To accommodate temperature dependence in kinetic parameters, the proposed analytical model is extended. We divided the 0–800 °C temperature range of the experimental TG/DTG data into equal intervals, each of which contains 20 °C variation. Using Eq. (10), E and T can be calculated for each temperature interval. The parameters set $E(T)$ and $A(T)$ was then obtained across all intervals and shown in Fig. 4. As the temperatures were divided into sufficiently small intervals, the discrete values of the kinetic parameters should be expressible as continuous functions of temperatures. Fig. 4 indicates that the variation of activation energy with temperature for oil shale at constant heating rate is so small that it can be neglected. We may conclude that for constant heating rate, it is reasonable to approximate the activation

Table 2

Comparison of the known true activation energies and estimated activation energies.

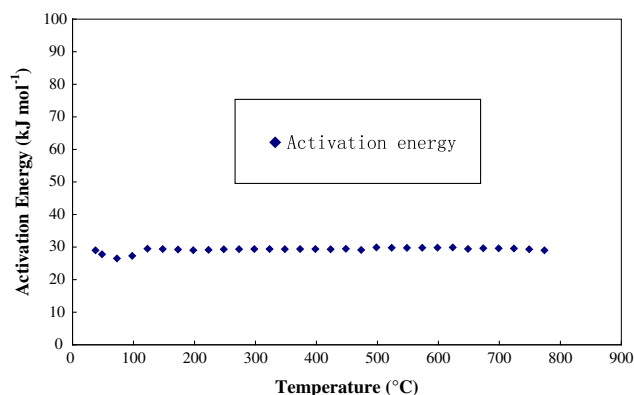| True E (kJ mol^{-1})	Estimated E (kJ mol^{-1})
60	60.12
150	150.10
300	300.22

Fig. 4. Effect of temperature variation on activation energy at constant heating rate.
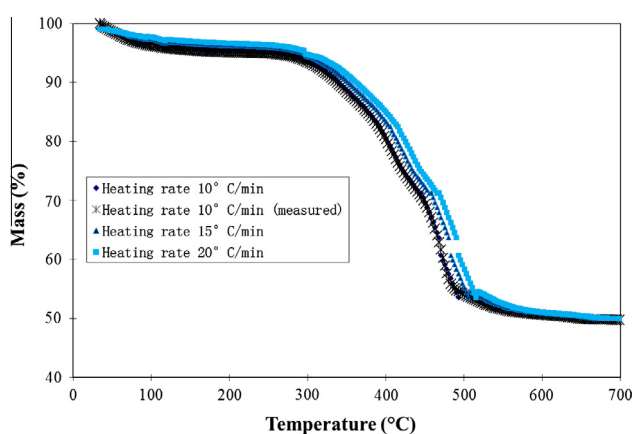

Fig. 5. Effect of heating rate on weight loss.

energy as being independent of the temperature, as most reports assume.

Furthermore, note that this proposed parameter estimate method can be also used to estimate both the reaction order and constant approximation of the kinetic parameter through calculating the mean of the set of estimated parameter values.

3.3.4. Investigation on kinetic mechanisms

After validation, the proposed model can be employed to investigate various kinetic mechanisms of pyrolysis, for example, the effects of kinetic parameters, such as the initial weight, heating rate and the final heating temperature. Fig. 5 shows such a simulation example. The results demonstrate that the peak rates of weight losses shift towards higher temperatures as the heating rates increase. However, heating rates have negligible effects on the simulated final weight losses.

3.3.5. Graphic determination of kinetic parameters

The proposed analytical model can be also used as a graphical version for determining kinetic parameters. For a small enough T_0 (can be obtained through subtraction of T_0 from T), Eqs. (9) and (10) can be approximated and rewritten as

$$\ln\left(\frac{-\ln(1-X)}{T^2}\right) = \ln\left(\frac{AR}{\beta(E+2RT)}\right) - \frac{E}{RT} \quad (13)$$

Using a plot of $\ln\left(\frac{-\ln(1-X)}{T^2}\right)$ against $1/T$ as a straight line though graph method, the slope gives activation energy E and the incept estimates pre-exponential factor A. It is worth mentioning that the obtained E and A from Eq. (13) are for each temperature interval ΔT. To obtain average values, we can add up all values and divide by

the number of temperature intervals. Similar deduction to an n-order reaction can be obtained also.

4. Discussion

Since an accurate Arrhenius type equation for modelling thermal decomposition kinetics of pyrolysis is inherently nonlinear allowing no exact analytical solution, the proposed method introduced an approximation to the solution. The approximation is minimal, accurate, efficient and simple which precisely captures the thermochemical mechanisms of oil shale pyrolysis. This paper makes three main improvements over the state-of-art pyrolysis models: (1) the innovative methodology for modelling pyrolysis kinetics based on analytical approximation which allows various extensions to accommodate more complex features in reaction models; (2) the analytical model which represents a significant simplification and efficiency of the kinetic calculation and analysis; (3) the robustness and high accuracy of the approach and model which capture the thermal decomposition kinetics of pyrolysis and allow for analytical estimates of kinetic parameters. Experimental and numerical validations show high accuracy of the model ($R^2 > 0.99$). Implementation is extremely simple.There is one question regarding to the proposed model. The model accuracy depends on the temperature interval ΔT. However, a relatively large temperature increment, for example, at least 25 °C (or even 50 °C, see Fig. 3), can be chosen for accurate results. The maximum allowable temperature interval for a desired accuracy needs further investigation.

5. Conclusions

This paper reports a novel method for modelling pyrolysis kinetics of oil shale which presents several methodological contributions to the current literature. Results approve that the proposed efficient model is suitable for simulation of pyrolysis kinetics of oil shale. Importantly, the new approach is based on general ideas and thus easily applicable to other more complex kinetic models. The developed methodology may be of assistance in modelling any type of fuel resources and reaction kinetics that follow Arrhenius equation. The developed model is simple, accurate, efficient, application-independent and computationally attractive. There is a need for such models in fuel and energy technology.

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